

## Unsaturated Esters of Sucrose

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Although the synthesis and polymerization of many unsaturated compounds have been described in recent years, relatively few investigations have been concerned with the preparation of monomers from sucrose. The only derivative that has received particular attention is allylsucrose,<sup>2</sup> which has potential use as a resistant, protective and decorative coating and adhesive. In our work with ether derivatives, we found that the polymerization of a heptaallylsucrose is promoted by replacing the remaining hydroxyl group with an unsaturated acyl residue such as the methacrylyl group.<sup>2c</sup> This work suggested the study of unsaturated esters, and this report describes the

preparation and properties of six unsaturated esters of sucrose, namely, methacrylyl, crotonyl, furoyl, cinnamoyl, undecylenoyl and allyloxycarbonyl.

While the preparation and polymerization of some monofunctional derivatives of these acids have been described in the literature<sup>3</sup> very little work on polyfunctional derivatives is on record.<sup>4</sup> In the carbohydrate field the methacrylates of glucose, maltose, dextrin and starch were described by Treadway and Yanovsky.<sup>5</sup> Outside of ill-characterized linoleic<sup>6</sup> and rosin<sup>7</sup> esters Oden's<sup>8</sup> preparation of cinnamoylsucrose is virtually the

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(2) (a) Tomecko and Adams, *THIS JOURNAL*, **45**, 2698 (1923); (b) Frey, Dissertation, Eidgenoss. Techn. Hochschule, Zurich, 1926; (c) Nichols and Yanovsky, *THIS JOURNAL*, **67**, 46 (1945); (d) Nichols and Yanovsky, *Sugar*, **42**, No. 9, 28 (1947); (e) Zief and Yanovsky, *Ind. Eng. Chem.*, **41**, 1697 (1949).

(3) Neher, *Ind. Eng. Chem.*, **28**, 267 (1936); Liebermann and Zsuffa, *Ber.*, **44**, 841 (1911); Sapiro, Linstead and Newitt, *J. Chem. Soc.*, 1784 (1937); Ross, Gebhart and Gerecht, *THIS JOURNAL*, **67**, 1275 (1945).

(4) Muskat and Strain, U. S. Patents 2,384,115, 2,384,120 (1945).

(5) Treadway and Yanovsky, *THIS JOURNAL*, **67**, 1038 (1945).

(6) Rosenthal and Lenhard, U. S. Patent 1,739,863 (1929).

(7) Rheineck and Rabin, U. S. Patent 2,077,371 (1937).

(8) Oden, *Arkiv Kemi Mineral. Geol.*, **7**, no. 15, 23 (1918).

TABLE I  
PROPERTIES OF UNSATURATED ESTERS OF SUCROSE

Octa substituted derivatives of sucrose	Formula	M. p., °C.	Yield, Sapon. equiv.			OH, %	Unreacted OH groups	[α] <sub>D</sub> <sup>20</sup> CHCl <sub>3</sub> <sup>a</sup>	n <sub>D</sub> <sup>20</sup>	Carbon, %		Hydrogen, %		Mol. weight calcd. for octa deriv.
			%	Calcd.	Found					Calcd.	Found	Calcd.	Found	
Methacrylyl	C <sub>44</sub> H <sub>84</sub> O <sub>19</sub>		54	111	106	0.6	0.3	+30.8	1.4847	59.60	59.39	6.09	5.99	886
Crotonyl	C <sub>44</sub> H <sub>84</sub> O <sub>19</sub>		95	111	114	.5	.2	+39.3	1.4980	59.60	59.80	6.09	6.12	886
Cinnamoyl <sup>b</sup>	C <sub>34</sub> H <sub>70</sub> O <sub>19</sub>	84-86	75	173	172.5	.0	.0	+11.6	....	72.93	72.77	5.07	5.19	1382
Furoyl <sup>c</sup>	C <sub>62</sub> H <sub>38</sub> O <sub>27</sub>	90-99	69	137	141	.3	.2	+48.2	....	57.04	56.85	3.47	3.76	1094
Undecylenoyl	C <sub>100</sub> H <sub>166</sub> O <sub>19</sub>		81	209	208	.0	.0	+21.0	1.4720	71.86	71.88	9.94	9.96	1670
Allyloxy-carbonyl	C <sub>44</sub> H <sub>84</sub> O <sub>27</sub>		34			.5	.2	+39.6	1.4778	52.07	51.92	5.32	5.43	1014

<sup>a</sup> All rotations cited are specific rotations of the D line of sodium at 25°. <sup>b</sup> Oden reported m. p. of 87-88°; [α]<sub>D</sub><sup>20</sup> 12.5. <sup>c</sup> Sintered at 88°; melted gradually over the range 90-99°.

TABLE II  
POLYMERIZATION OF SUCROSE ESTERS

	Gelation time (1% benzoyl peroxide, 100°)	Gelation time (blowing with O <sub>2</sub> , 100°), min.	Original viscosity (100°), centistokes	Physical appearance after copolymerization for 24 hr. with equal quantities of styrene methyl methacrylate	
Methacrylyl	3 min.	30 (heating alone)	Polym. during visc. meas.	Clear hard glass	Clear hard glass
Crotonyl	4.5 hr.	327	218.4	Clear hard glass	Clear hard glass
Allyloxycarbonyl	18 hr.			Heterogeneous gel	Heterogeneous gel
Undecylenoyl	Slight incr. visc. in 36 hr.	349 visc. then 40.5 centistokes	14.3	Heter. visc. liq., colorless solid	Heterogeneous gel
Furoyl	{ No change in 48 hours			Heterogeneous gel	Heterogeneous gel
Cinnamoyl				Clear hard glass	Opaque solid

only reference to a pure octa substituted unsaturated ester of sucrose.

The methacrylyl and crotonyl esters were prepared by esterification of sucrose with the corresponding anhydride in pyridine; the cinnamoyl furoyl, undecylenoyl and allyloxycarbonyl derivatives were obtained from the appropriate acid chloride. The yellow cinnamoyl and colorless furoyl derivatives were amorphous solids. The colorless methacrylyl and allyloxycarbonyl, the yellow undecylenoyl and the viscous brown crotonyl derivatives were liquids. Because the relatively high molecular weights of these products paralleled high boiling points, the liquids were not distilled. Impurities were removed by washing chloroform solutions of the derivatives with dilute acid, sodium bicarbonate and finally with water. The fairly good agreement of the saponification equivalents with the theoretical values given in Table I indicates that the products were substantially pure. Practically complete substitution took place in all cases.

Small samples of each ester were heated with 1% of benzoyl peroxide at 100° in an atmosphere of nitrogen. The esters also were "blown" with oxygen (a stream of gas was bubbled through the ester at a measured rate), as well as copolymerized with styrene and methyl methacrylate at 100°. Table II records all the changes observed. As expected, the methacrylyl derivative was the most reactive in peroxide-catalyzed polymerization. The crotonyl and allyloxycarbonyl derivatives showed less reactivity and undecylenoyl exhibited

feeble activity. After twenty-four hours, furoyl and cinnamoylsucrose had formed a molten mass and, upon cooling, the brittle products were completely soluble in acetone at room temperature. The hard, colorless gels obtained from methacrylyl, crotonyl and allyloxycarbonyl derivatives were insoluble in organic solvents.

Acrylylsucrose would be expected to polymerize rapidly, since acrylates polymerize faster than methacrylates, but attempts to prepare monomeric acrylylsucrose from acrylyl chloride were unsuccessful. In this Laboratory, it has been exceedingly difficult to prepare pure polyacrylates from polyhydroxy compounds. Gelled materials were also obtained in attempts to prepare a conjugated acid derivative from sorboyl chloride.

The methacrylyl derivative gelled within thirty minutes when heated at 100°. At room temperature, a 50% solution in toluene containing 1% benzoyl peroxide gelled within sixteen days. Within this time, a 50% toluene solution containing 0.1% cobalt octoate deposited a smaller quantity of gelled material. A control solution remained unchanged. The cobalt octoate experiment indicated that methacrylylsucrose readily undergoes oxidative polymerization as well as additive polymerization. Tack-free, clear films from 50% toluene solutions were obtained by heating coated glass panels at 100° for five hours. Crotonylsucrose gave films that dried more slowly.

It then seemed of interest to determine whether these esters would form homogeneous copolymers

readily with highly reactive monomers, such as styrene and methyl methacrylate. Methacrylyl and crotonyl derivatives gave hard, clear, insoluble and infusible copolymers. Cinnamoylsucrose, copolymerized with styrene, also yielded a hard, clear resin insoluble in organic solvents. Furoylsucrose was easily extracted with acetone from mixtures with styrene and methyl methacrylate. The allyloxycarbonyl and undecylenoylsucrose mixtures were cloudy.

The behavior of crotonyl and cinnamoylsucrose was rather interesting. Inasmuch as the polymerization of simple alkyl esters of cinnamic acid has been reported, the failure of cinnamoylsucrose to polymerize seemed surprising. Cinnamoylsucrose, however, gave a clear, hard copolymer with styrene. Though the polymerization of monofunctional crotonyl esters has not been described, crotonylsucrose polymerizes readily under the identical conditions used for cinnamoylsucrose. Crotonylsucrose, like methacrylylsucrose, copolymerized rapidly with styrene and methyl methacrylate. In sharp contrast to the crotonyl derivative, the eight furoyl groups in furoylsucrose showed no tendency to take part in copolymerization or polymerization reactions.

### Experimental

**Starting Materials.**—Methacrylic anhydride was redistilled in the presence of hydroquinone immediately before use. The fraction boiling at 65° (2 mm.) was saved. Crotonic anhydride, kindly supplied by the Carbide and Carbon Chemicals Corporation, was used without further purification. Undecylenoyl chloride, prepared according to English and Velick,<sup>9</sup> was distilled at 102° (2 mm.). Cinnamoyl chloride, prepared from the acid and phosphorus trichloride according to the method of Griffin and Nelson,<sup>10</sup> was distilled at 125–127° (9 mm.). Allyl chloroformate, kindly supplied by the Hooker Electrochemical Co., was redistilled before use.

**Esterification Method.**—Finely powdered sucrose (17.1 g., 0.05 mole) and pyridine (75 cc., 0.93 mole) were placed in a 250-cc. three-necked flask equipped with a stirrer, reflux condenser and dropping funnel. The acylating agent (4.4 moles) was added slowly, with rapid stirring.

**Methacrylylsucrose.**—Methacrylic anhydride containing 0.01% hydroquinone was added at 70–75°. After the reagents were mixed, the flask was heated at 80–90° for five hours and was then left overnight at room temperature. The reaction product, plus some undissolved sucrose, was poured in a thin stream into ice-water, accompanied by vigorous stirring. The sticky, colorless sirup that separated was washed several times with water and was then dissolved in chloroform. The chloroform solution was washed twice with cold dilute sulfuric acid, twice with dilute sodium bicarbonate, and finally with distilled water until the aqueous layer was neutral. The chloroform layer was separated, dried over anhydrous sodium sulfate, decolorized with activated carbon, then concentrated *in vacuo* under nitrogen. After traces of solvent were removed by heating at 100° (1 mm.), a mobile colorless sirup was obtained. Attempts to crystallize the sirup were unsuccessful. In one experiment, cuprous chloride was added in place of hydroquinone as a polymerization inhibitor; it proved to be troublesome to separate from the product without distillation.

**Crotonylsucrose.**—With crotonic anhydride under identical conditions, except for the omission of hydroquinone, all the sucrose dissolved during heating at 80–90°. The

same method of purification gave a much higher yield of a brown, viscous sirup.

**Undecylenoylsucrose.**—The procedure was essentially that of Hess and Messmer.<sup>11</sup> A solution of undecylenoyl chloride in 50 cc. of chloroform, added at room temperature, deposited a colorless precipitate. Upon gradual warming, the precipitate disappeared, and two layers appeared. After heating and subsequent cooling, the lower layer solidified (pyridine hydrochloride plus undecylenoyl chloride–pyridine complex). The upper layer was separated and treated with ether until a precipitate no longer separated. The ethereal layer was filtered, then concentrated *in vacuo*. After the residue was dissolved in chloroform and worked up as previously described, a pale-yellow oil was obtained.

**Cinnamoylsucrose.**—Cinnamoyl chloride in 50 cc. of chloroform was added at room temperature. After heating and the standard purification procedure, the chloroform layer was concentrated *in vacuo* to 50 cc. Absolute ethyl alcohol was added until the first sign of permanent turbidity. Upon standing for forty-eight hours, a gum separated. Concentration of a chloroform solution of this gum gave a yellow, friable, powdery solid. The product was further purified by two more precipitations from chloroform by ethyl alcohol.

**Furoylsucrose.**—After furoyl chloride had been added at 0°, the reaction mixture was stirred at room temperature for seven hours, and was then allowed to stand overnight. The purple solution was poured, with stirring, into ice-water. The air-dried precipitate was dissolved in acetone, decolorized, and poured again, with stirring, into ice-water. The dried powder sintered at 88°, and melted at 90–99°.

**Allyloxycarbonylsucrose.**—Allyl chloroformate was added at 0° according to Muskat and Strain's method<sup>7</sup> of preparing polymerizable carbonates. Pyridine (25 cc.) was added to the solid mass. The mixture was then allowed to reach room temperature. After standing for forty-eight hours, the mixture was stirred for three hours, poured in a thin stream into water and worked up as for methacrylylsucrose. A low yield of a thick, colorless sirup was obtained.

**Polymerization of Esters.**—Small quantities (0.5 g.) of each of the esters were weighed into 4-inch test-tubes which had been previously flushed with nitrogen, and 1% of benzoyl peroxide was added. The tubes were then flushed with nitrogen once more, stoppered, and placed in an oil-bath kept at 100°.

**Blowing of Esters.**—A modified Ostwald pipet containing 7.2 cc. of the ester was placed in an oil-bath at 100°. When thermal equilibrium was attained (ten minutes), oxygen was bubbled through the ester at a rate of 7.5 liters per hour. The rate was determined by a flowmeter calibrated by a wet test meter.

**Copolymerization of Esters.**—Small quantities (0.5 g.) of the esters and equal weight of methyl methacrylate or freshly distilled styrene were mixed in small test-tubes. One per cent. of benzoyl peroxide, based on the total monomer weight, was added, and the test-tubes were flushed with nitrogen, tightly stoppered and heated at 100° as above.

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### Summary

Six unsaturated esters of sucrose, namely, the methacrylyl, crotonyl, furoyl, cinnamoyl, undecylenoyl and allyloxycarbonyl derivatives were prepared, and some of their properties were determined.

Polymerization of these esters at 100° in the

(9) English and Velick, *THIS JOURNAL*, **67**, 1413 (1945).

(10) Griffin and Nelson, *ibid.*, **37**, 1563 (1915).

(11) Hess and Messmer, *Ber.*, **54**, 499 (1921).

presence of 1% benzoyl peroxide was studied. Methacrylylsucrose is the most reactive, undecylenoysucrose is slightly reactive, the crotonyl and allyloxycarbonyl derivatives show intermediate reactivity; furoylsucrose and cinnamoysucrose

do not polymerize at all.

Copolymerization of these esters with styrene and methyl methacrylate in the presence of 1% benzoyl peroxide also was studied.

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